

Determination of Hexavalent Chromium Fractions in Plastics Using Laboratory-Based, High-Resolution X-ray Emission Spectroscopy

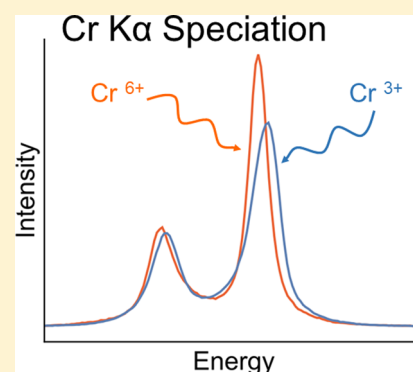
Evan P. Jahrman,[†] Gerald T. Seidler,^{*,†} and John R. Sieber[‡]

[†]Physics Department, University of Washington, Seattle, Washington 98195-1560, United States

[‡]Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8391, United States

Supporting Information

ABSTRACT: Cr(VI) is a well-known human carcinogen with many water-soluble moieties. Its presence in both natural and man-made substances poses a risk to public health, especially when contamination of groundwater is possible. This has led the European Union and other jurisdictions to include Cr(VI) in restriction of hazardous substances regulations. However, for several important industrial and commercial purposes, analytical capability to characterize Cr(VI) is known to be insufficient for regulatory purposes. For example, advanced X-ray spectroscopies, particularly synchrotron-based X-ray absorption fine structure (XAFS) studies, have shown that species interconversion and under-extraction can be difficult to prevent in many existing liquid extraction protocols when applied to plastics, mining ores and tailings, and paint sludges. Here, we report that wavelength dispersive X-ray fluorescence spectroscopy taken at energy resolutions close to the theoretical limit imposed by the core-hole lifetime, generally called X-ray emission spectroscopy (XES) in the synchrotron community, can be used in the laboratory setting for noninvasive, analytical characterization of the Cr(VI)/Cr ratio in plastics. The selected samples have been part of ongoing efforts by standards development organizations to create improved Cr(VI) testing protocols, and the present work provides a direct proof-of-principle for the use of such extremely high-resolution laboratory WDXRF as an alternative to liquid extraction methods for regulatory compliance testing of Cr(VI) content. As a practical application of this work, we report a value for the Cr(VI) mass fraction of the new NIST Standard Reference Material 2859 Restricted Elements in Polyvinyl Chloride.



Chromium is an earth-abundant element whose toxicity, mobility, and bioavailability are all heavily dependent on its oxidation state within a given compound. The more harmful species, hexavalent Cr, i.e., Cr(VI), is known to be roughly one hundred times as hazardous as trivalent Cr(III) due to its carcinogenic properties.¹ It is therefore critical that test methods be in place to understand the speciation of Cr in our environment and in manufactured products. Indeed, the Cr(VI) concentration in the latter can be the result of unidentified precursors and subject to change following heat treatments or the incorporation of chemically active agents during processing.² Consequently, standard protocols for Cr(VI) characterization have been developed by several international organizations with the goal of meeting restriction of hazardous substances (RoHS) guidelines mandating a maximum mass fraction of Cr(VI) of 0.1% in materials used in consumer goods including plastics.³ Further milestones have been set for the development of standard test materials and procedures for improved Cr(VI) detection with the goal of mitigating the risk of public exposure to Cr(VI) and a consequent reduction in adverse human health outcomes as motivated by established hazard control strategies.⁴

Methods capable of determining Cr(VI) content within a solid sample matrix currently exist but they suffer from systematic and pragmatic shortcomings. Many benchtop

procedures require a chemical extraction process to separate Cr(VI) prior to colorimetric analysis by reaction with diphenyl carbazide.⁵ As a result, wet chemical methods are often criticized for susceptibility to species interconversion and incomplete extraction.

Indeed, a study by Malherbe et al. demonstrated the tendency of EPA method 3060a to systematically underestimate the mass fraction of Cr(VI) in a series of reference soils.⁶ This study implemented an X-ray spectroscopic technique, X-ray absorption fine structure (XAFS), that has the advantage of minimal sample preparation requirements so the electronic structure of a species may be interrogated in its native environment. In the case of Cr, the highly distinctive pre-edge feature is directly sensitive to the coordination and oxidation state of the metal within a given compound.⁷ Moreover, XAFS is a robust methodology that has previously been applied to studies of Cr in glasses,⁸ soils,⁹ plastics,¹⁰ coals,^{11,12} chrome-tanned leathers,¹³ and ultramafic rocks.¹⁴ However, to play a significant role in environmental and industrial regulatory monitoring and compliance verification, a technique must be highly accessible to its intended users. While

Received: January 19, 2018

Accepted: May 15, 2018

Published: May 15, 2018



Table 1. Selected Details of Measured Plastics^a

| sample | supplier ^b | polymer | Cr mass fraction (mg/kg) | Cr(VI)/Cr from preparation (%) | Cr(III) source | Cr(VI) source |
|-------------------------|-----------------------|---------|--------------------------|--------------------------------|--------------------------------|---|
| P106 ⁴⁴ | CCQM | PP | 252.5 ± 6.8 | 100 | | BaCrO ₄ /PbCrO ₄ |
| ES ⁴³ | IEC TC111 | PVC | 1740 ± 350 | 100 | | PbCrO ₄ |
| F6 ⁴³ | IEC TC111 | PVC | 670 ± 130 | 100 | | PbCrO ₄ |
| SRM 2859 ⁵⁸ | NIST | PVC | 716 ± 16 | 100 | | Na ₂ Cr ₂ O ₇ ·2H ₂ O |
| SRM 2861 ⁵⁹ | NIST | PVC | 50.4 ± 3.1 | 100 | | Na ₂ Cr ₂ O ₇ ·2H ₂ O |
| EC681k ⁶⁰ | IRMM | PE | 100 ± 5 | 24.6 | Cr ₂ O ₃ | PbCrO ₄ |
| CRM 8113a ⁶¹ | NMIJ | ABS | 943.6 ± 18.0 | 25.1 | Cr(III)-acetylacetonate | PbCrO ₄ |
| CrS15 | NIST | PE | 514.8 ± 2.2 | 0 | Cr(III)-benzoylacetate | |

^aThe samples contained various Cr compounds compounded in polymers: polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), and acrylonitrile butadiene (ABS). The identity of the supplier, mass fraction and incorporated chromium compounds is also provided. For each Cr mass fraction value, the corresponding uncertainty is representative of a 95% confidence interval. Materials, values, and uncertainty estimates are discussed in detail in the [Supporting Information](#). ^bOrganizations include the Inorganic Analytical Working Group of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM), the International Electrotechnical Commission Technical Committee 111 (IEC TC 111), the National Institute of Standards and Technology (NIST), the Institute for Reference Materials and Measurements (IRMM), and the National Metrology Institute of Japan (NMIJ).

there has been a resurgence of interest in laboratory-based XAFS,^{15–19} at present XAFS analysis of extremely dilute samples is restricted to synchrotron light sources. Despite a growing number of beamlines serving industrial clients, synchrotron efforts are not currently a practical solution for high-throughput, fast turn-around, routine characterizations that are the workhorse needs of the broader analytical chemistry community.

However, there exist higher-access X-ray spectroscopic techniques having the same advantages of sensitivity to electronic structure, nondestructive measurement, and robustness to sample matrix. For example, X-ray photoelectron spectroscopy (XPS) is an established technique capable of speciation studies, yet is traditionally surface-sensitive and requires an ultrahigh vacuum often incompatible with plastics, epoxies, and resins. However, X-ray fluorescence (XRF) spectroscopy, which examines the difference in screening between two core holes, is widely implemented as a laboratory-based technique for elemental analysis. When equipped with sufficient energy resolution, such as in wavelength dispersive X-ray fluorescence (WDXRF) studies, measurements begin to demonstrate sensitivity to speciation. Numerous authors assert the viability of assigning coordination, and thus rudimentary speciation, according to the relative intensities of characteristic fluorescence lines.^{20–22} In the case of Cr, branch-ratio analysis has been demonstrated to possess some limited utility in the detection of the hexavalent species.²³

Further and more reliable determinations from WDXRF are pursued by instead investigating the fine shape of individual spectral features. Previously, Baydas et al.²⁴ reported the sensitivity of the Cr K α fluorescence line to speciation via WDXRF, but while their results are promising, the utilized instrumentation possessed insufficient energy resolution to resolve peaks split due to spin–orbit coupling, let alone more subtle effects. A recent WDXRF study in the K β region satisfactorily resolved spectral features such that hexavalent and trivalent species were noticeably distinct, but suffered from limitations in energy range and energy resolution that complicated background subtractions and decreased the total information content of the spectra.²⁵

The point of the present paper is to improve the performance of WDXRF speciation of Cr by refining the energy resolution of the measurements down to the intrinsic limit imposed by the core-hole lifetime of the principal 1s

photoexcitation of the Cr ion. Such extremely high resolution WDXRF is typically called X-ray emission spectroscopy (XES) in the synchrotron community,²⁶ and it has demonstrated capability for ascertaining several categories of local electronic and structural information that is not available from studies having coarser energy resolution.^{27–29} With growing frequency, XES is applied to studies of oxidation state, spin-state, covalency, or ligand environment, and like XAFS, XES is generally applicable to a range of sample environments.^{30–32} Accordingly, both experimental and theoretical works have investigated the viability of XES in the K β region as a tool for speciation studies of Cr in its native environment.^{33,34}

While previous XES studies of Cr(VI)/Cr speciation were performed at synchrotron light sources, we show here that recent technical advances have made such extremely high resolution WDXRF studies of dilute samples accessible in a laboratory setting. For completeness, we note that there is growing literature on lab-based XES instrumentation.^{17,35–42} In this work, using a low-powered, lab-based X-ray emission spectrometer,¹⁸ we perform Cr K α XES in a broad survey of reference-standard plastics based on various polymer formulations, Cr mass fractions, and prepared Cr(VI) species fractions. Previous XES studies report the Cr K β lines' speciation dependence,^{25,33,34} but here we find that the fine spectral changes between various oxidation states of Cr are adequately resolved to serve as references when fitting the stronger Cr K α spectrum of a plastic with unknown Cr content. This procedure yields quantitative results of the Cr(VI) species fraction consistent with a synchrotron XAFS study. Accordingly, we use the K α lines as they are the most intense transition available and consequently decrease necessary integration times and increase our sensitivity. These results strongly support the accuracy of using Cr K α for the purpose of determining the Cr(VI)/Cr ratio in plastics.

METHODS

Materials and Preparation. This study investigates several certified reference materials and laboratory-prepared blends selected to span a range of plastic polymer formulations, total Cr mass fractions, Cr(VI) species fractions, and Cr starting materials. In particular, the range of total Cr and Cr(VI) mass fractions was selected to encompass the typical ranges found in plastics and the allowable levels listed in regulations, respectively. This information is summarized in [Table 1](#)

where sample notation follows prior work or organizational convention.^{43,44} Of note, polypropylene (PP) P106 was selected to demonstrate that Cr(VI) may be processed without reduction; conversely, Cr515 was chosen to assess the capability of XES for detecting the presence of strictly trivalent Cr. EC681k and CRM 8113a were included as representative plastics containing a mixture of hexavalent and trivalent Cr in polyethylene (PE) and acrylonitrile butadiene styrene (ABS), respectively. The remaining samples were included to assess the robustness of the method for the photosensitive case of polyvinyl chloride (PVC). An advantage of XES is that minimal sample preparation is required, nonetheless, some samples were sectioned to be more easily positioned in the instrument. IEC TC 111's E5 and F6 materials were received as flat sheets that were cut into disks. SRM 2859 and SRM 2861 were pressed into flat disks. P106 and Cr515 were provided as thick disks from which approximately rectangular strips were cut. EC681k and CRM 8113a were provided as thin pellets that could be conveniently measured without sectioning.

XES Instrumentation and Methodology. The Seidler group at the University of Washington has recently developed laboratory-based (i.e., nonsynchrotron) X-ray emission spectroscopy (XES) instrumentation that provides signal-to-noise, energy resolution, and stability fully comparable to synchrotron-based instrumentation.^{16,18,45} These features make the instrument well-suited for studies of dilute samples. The technical design of the spectrometer is described in detail elsewhere.¹⁸ The present implementation employed an X-ray tube (Moxtek Au anode) operated at 40 kV and 200 μ A, i.e. only 8 W total tube power, a Ge (422) spherically bent crystal analyzer (SBCA) from XRS Tech, and an energy-dispersive silicon drift detector (Amptek SDD-X123), yielding exceptionally low backgrounds. In contrast to the prototype version of the instrument,¹⁸ we replaced the 2-axis tilt, using instead the azimuthal orientation method of Mortensen et al.,⁴⁵ and we removed the translational stage beneath the optic in favor of a passive mechanical system coupling the source and SBCA to rest on the 1-m diameter Rowland circle.

All hexavalent and trivalent Cr compounds used in the production of the selected plastics were measured to acquire reference spectra. In addition, the Cr $K\alpha$ spectrum of a 25 μ m thick stainless-steel shim was frequently collected to ensure a consistent energy scale throughout the study and to aid in the alignment of the plastic samples. While alignment in the spectrometer is achieved by laterally translating the sample behind the entrance slit until a maximum count rate is reached, this procedure was not possible given the low Cr contents present in the plastic samples. Rather, the stainless-steel shim was first aligned and then replaced by the plastic sample with an appropriate adjustment for changes in sample thickness and attenuation length. Note that this alignment need not be especially precise, as has been documented in Mortensen et al.¹⁶

Further care was needed to determine the Cr(VI) species fraction for samples that exhibited radiation damage.^{46,47} This was addressed in the standard way with a sample spinner to distribute the radiation dose over a larger sample area. Specifically, the spinner distributed the dose over an area approximately 28 times larger in size than that of the static sample. The scans averaged to represent the sample were then limited to those occurring before noticeable change in spectral shape or measured Cr(VI) content. The latter was assessed by examining the Cr(VI) fraction as a function of scan number and

selecting consecutive points statistically consistent with no photoinduced reduction. As a result, the first eight scans were used for all PVC materials for which a quantitative result is reported.

XAFS Synchrotron Methods. Cr K-edge X-ray absorption fine structure (XAFS) was measured at beamline X23A2 at the National Synchrotron Light Source (NSLS). Cr XAFS spectra were collected in fluorescence mode using a four-element Si drift detector (Hitachi Vortex EX). The primary beam was monochromatized using a Si (311) double-crystal monochromator and was collimated to a line shape approximately 300 μ m high and 9 mm wide. Each XAFS scan proceeded in 1 eV steps from 5889 to 5939 eV, 0.5 eV steps from 5939 to 5962 eV, 0.07 eV steps from 5962 to 6004 eV, 0.5 eV steps from 6004 to 6029 eV, and 2 eV from 6029 to 6338 eV with a 0.5 s dwell time at each point. Samples in powder form were prepared by cryogenic milling and mounted in a polyethylene sample cell between layers of 4 μ m thick polypropylene film (Somar Spectrolene). Plastic disks were prepared by melt pressing. Temperatures for melt pressing were kept well below those used for extrusion or complete melting of the sample; rather, the employed temperature was the minimum required to fuse the materials with the aid of a hydraulic press. Each sample was mounted on a spinner and rotated during measurements to overcome potential heterogeneity and to minimize potential beam damage. No evidence of beam damage was observed.

Fit Procedures. Determination of the Cr(VI) fraction by XES was accomplished via a least-squares regression analysis. First, the trivalent and hexavalent reference spectra were background corrected and normalized to the total number of counts in the integration range. The reference spectra were then fit to a pair of interpolating functions. Next, the spectrum of a sample with unknown chromium speciation was likewise background corrected and integral normalized. The portion of the unknown spectrum between 5400 and 5420 eV was fit by a linear combination of the interpolating functions representing the reference spectra. The fit was performed using the NonlinearModelFit function in Mathematica with the Cr(VI) species fraction as the optimization parameter, which was subsequently extracted along with its uncertainty.

Other sources of uncertainty affecting the fit were quantified, these include the particular choice of reference spectra and the variability in the XES energy scale upon sample exchange. The bias introduced with the choice of reference compound was estimated by performing fits with all possible combinations of references and calculating a corresponding uncertainty in the result. Additionally, the bias accompanying the imperfect reproducibility of the XES energy scale was estimated by sampling the maximal energy shifts introduced by sample exchange reported elsewhere.^{16,48} This was done by displacing an employed reference spectrum 10 meV lower, not at all, or 10 meV higher in energy. Displacements were done to both the trivalent and hexavalent references, and after considering all nine possible permutations, the standard deviation of the resulting fit parameters was taken as the resulting uncertainty.

For the XAFS data, the Cr(VI) fraction was determined from the near-edge region by analysis with the ATHENA software, version 0.9.25.⁴⁹ After fitting the edge shape to an error function, the pre-edge features were fit to a set of three Lorentzian functions. The choice of three features is in accordance with previously reported spectra and fit procedures,^{50–53} while the choice of Lorentzian functions is consistent with the work of Lytle et al.⁵⁴ and Calas et al.⁵⁵

The percentage of the hexavalent Cr species present in the plastic samples was related to the area of the Lorentzian of intermediate energy.^{50,53,56}

The uncertainty in the XAFS fitting procedure's result was estimated from successive scans of each compound. In the trivalent and hexavalent cases, these spectra were merged prior to fitting. However, this was not done for the plastic compounds to minimize sensitivity to the precise background and normalization treatment applied to the necessarily dilute samples. Rather, all features were fit to a single scan before fixing all parameters, except the height of each feature. The regression analysis was then applied to the remaining scans and a result with a corresponding uncertainty obtained. This uncertainty was propagated with the error in the intensity of the Lorentzian representing 3d → 4p mixing in the hexavalent reference as obtained by the fitting procedure.

RESULTS AND DISCUSSION

Reference compound spectra are presented in Figure 1. Comparing the trivalent and hexavalent Cr compounds,

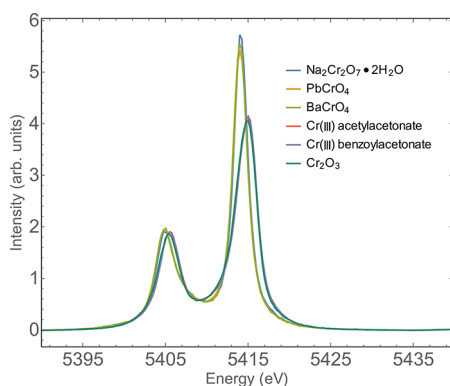


Figure 1. Cr $K\alpha$ XES of selected trivalent and hexavalent reference Cr compounds after background correction and integral normalization. Note, the spectrum of Cr(III) acetylacetonate is nearly identical to that of Cr(III) benzoylacetonate, and therefore hidden from view.

differences in the spectral features are easily discernible with the current energy resolution and a determined instrumental sample-to-sample reproducibility of better than 20 meV. The trivalent species possess additional electron density in valence states, yielding additional screening of the nuclear potential and an increase in (2p,3d) exchange in the final electronic configuration. The spectral features of the trivalent species are consequently shifted to higher energy and broadened with respect to the hexavalent species.²⁹ From Figure 1, it is apparent the $K\alpha$ emission probes an extremely local component of the electronic structure due to the involvement of only deeply bound orbitals. Nonetheless, minute differences are seen between the spectra of various species due to covalency and crystal field effects. For that reason, it is important to compare a spectrum of interest to that of reference compounds representative of the electronic structure of Cr(VI) and Cr(III) atoms in the sample and to assess possible systematic errors related to this choice. As a step in this direction, Figure S1 of the Supporting Information (SI) shows residual spectra within the families of Cr(III) and Cr(VI) reference materials, while Table S3 lists the position and intensity of the maxima of each reference material's Cr $K\alpha$ emission lines.

The main results of the study are presented in Figure 2 and Table 2. In Figure 2, we present the spectra collected from the

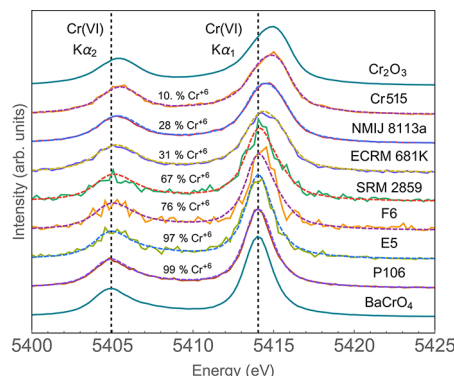


Figure 2. Vertically offset Cr $K\alpha$ XES spectra of plastics bracketed by compounds of pure-end member species (trivalent Cr_2O_3 , top; hexavalent BaCrO_4 , bottom). The measured spectrum for each plastic is shown along with the fit (dashed) provided by a least-squares regression analysis and the percent Cr(VI) determined from the fit. The first 10 eV and last 15 eV, which were collected to properly correct for background, are omitted. Note that all spectra are background corrected and integral normalized. For ease of reference, vertical dashed lines pass through the center of the Cr $K\alpha_1$ and $K\alpha_2$ peaks in BaCrO_4 .

reference plastics, least-squares fits to a linear superposition of reference compound spectra, and labels indicating the inferred Cr(VI) fraction. For plastics other than PVC, the Cr sources used in the production process were selected as references with PbCrO_4 selected for the case of P106; however, fits to strictly BaCrO_4 (Cr(VI)) and Cr_2O_3 (Cr(III)) were employed in the PVC samples for convenience. Among other details, Table 2 presents the Cr(VI) species fractions determined by XES and their corresponding uncertainties. This final error estimate was calculated by propagating the magnitude of each source of bias reported in Table S1. Note that Table 2 also contains an estimate of the Cr(VI) mass fraction which was calculated from the estimated Cr(VI) species fraction and the total Cr mass fraction known from the preparation procedure or certified value for each material. When the Cr(VI) mass fraction is desired and the total Cr mass fraction is unavailable, this technique would require determination of total Cr by an appropriate method, such as XRF or inductively coupled plasma optical emission spectrometry (ICP-OES).

The Cr(VI) species fractions measured by other spectroscopic techniques, including XAFS, are shown in Table 2. Furthermore, representative results of the fits in the near-edge region of the XAFS spectra are shown in Figure 3, while the remaining fitted systems are presented in Figure S2. In general, the XAFS and XES methods are consistent with each other and with known preparation conditions. However, the XES results overestimate the Cr(VI) content with respect to XAFS in the limit of strictly trivalent Cr, as in Cr_2O_3 . This can be explained by differences between the collected plastic sample's spectrum and that of the reference. The fit procedure is then unable to relax the fit onto the strictly trivalent case and consequently overestimates the present Cr(VI) content. This can be seen in greater detail in Table S2, which shows using Cr(III) benzoylacetonate as the trivalent fit component leads to a significantly larger estimation of the Cr(VI)/Cr species fraction than using Cr(III) oxide as the trivalent reference compound.

Table 2. Species Fractions Determined by XAFS and XES are Presented along with Total Integration Times for the Latter^a

| sample | Cr(VI)/Cr from preparation (%) ^c | Cr(VI)/Cr by colorimetry (IEC 62321–7–2) (%) | Cr(VI)/Cr by XAFS (%) | Cr(VI)/Cr by XES (%) | integration time in XES (h) | Cr(VI) mass fraction by XES (mg/kg) |
|-----------------------|---|--|-----------------------|----------------------|-----------------------------|-------------------------------------|
| P106 | 100 | | 100.0 ± 1.6 | 99.4 ± 2.5 | 86.1 | 250.9 ± 7.2 |
| E5 | 100 | 73.6 | | 96.8 ± 3.8 | 5.3 | 1680 ± 180 |
| F6 | 100 | 63.0 | | 75.9 ± 6.6 | 5.3 | 508 ± 67 |
| SRM 2859 | 100 | | | 67.0 ± 4.5 | 5.3 | 480. ± 33 |
| EC681k | 24.6 | | 22.4 ± 1.8 | 30.5 ± 3.6 | 73.3 | 30.5 ± 3.7 |
| CRM 8113a | 25.1 | | 30.3 ± 1.2 | 28.1 ± 3.5 | 44.4 | 265 ± 33 |
| Cr515 | 0 | | 3.1 ± 0.5 | 10.2 ± 4.3 | 30 | 52 ± 22 |
| SRM 2861 ^b | 100 | | | 0 | | 0 |

^aThe Cr(VI) mass fraction was calculated from the Cr(VI) species fraction and total Cr mass fraction. In the case of E5 and F6, the results of an interlaboratory study facilitated by IEC TC 111 to determine the hexavalent chromium content via colorimetric analysis⁴³ are also included. Uncertainty estimates provided for the Cr(VI) mass fractions by XES are combined standard uncertainties including the uncertainty of the assigned total Cr value and the uncertainty of the found Cr(VI)/Cr ratio. All uncertainty values represent one standard deviation. ^bSee SI for an explanation of this result. ^cSee text for discussion of interconversion during preparation.

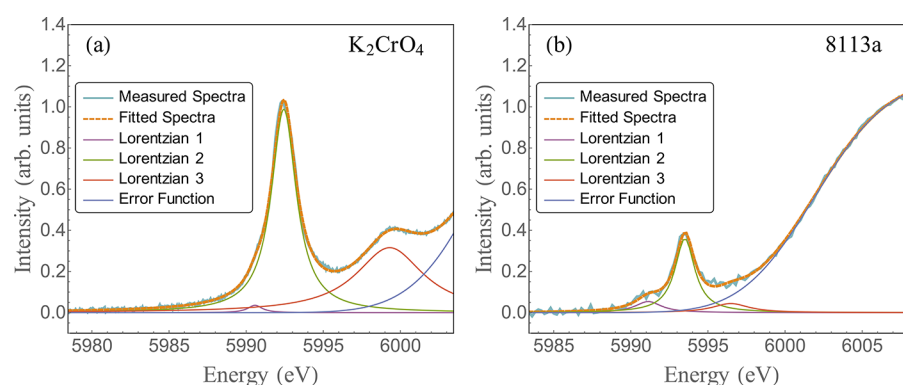


Figure 3. Near-edge region of (a) the XAFS spectra of the hexavalent reference, potassium chromate, and (b) CRM 8113a, a certified reference material developed for heavy metal analysis with respect to RoHS directives. Also shown are the acquired fits and their components.

However, iteratively displacing the position of the reference compound spectra, as in Table S1, leads to minimal changes in the resulting Cr(VI)/Cr species fraction. This suggests that either XES analysis does in fact overestimate Cr(VI) content in the strictly trivalent case or the electronic structure of the measured trivalent chromium is no longer well represented by Cr(III) benzoylacetone.

A similar bias is observed at low Cr(VI) content in the XAFS results where the intensity of the peak nominally assigned to a $1s \rightarrow 3d$ transition is related to the presence of Cr(VI). Additional peaks are present in the pre-edge region, including a peak on the low energy side of the transition of interest. As noted by Szulcowski et al.,⁵³ this peak becomes particularly noticeable in predominantly Cr(III) samples. Distinguishing these peaks, as well as reliably fitting a peak to a feature of now minimal intensity, thus complicates the fit procedure at low Cr(VI) content. Furthermore, strictly hexavalent Cr sources were employed in the production of materials E5, F6, SRM 2859, and SRM 2861, yet the XES measurements often reveal these materials to be reduced and to a lesser degree than reported by colorimetric analysis. Likely physical sources of reduction include processing and extrusion at 175 °C, the presence of Sb in F6 and SRM 2861, and the presence of stabilizer and plasticizer compounds in SRM 2859 and SRM 2861,^{2,43} while species interconversion or incomplete extraction during preparation for colorimetric analysis can contribute to under-estimation of Cr(VI).

As a final point of data analysis, it is useful to evaluate the residuals of the fits, see Figure S3. The deviations from Poisson

noise are minimal and are of the same general scale as the intrafamily variations of the Cr(III) and Cr(VI) reference materials, presented in Figure S1. Furthermore, Table S1 shows that, although the choice of reference is a significant contribution to the net error in an estimate of the hexavalent species fraction, it amounts to not more than 2% to 4% relative uncertainty. These results and the spectra shown in Figure 1 provide evidence that Cr $K\alpha$ emission is relatively insensitive to electronic structure differences among materials of the same oxidation state, as is required for robust species fractionation estimates.

The above results present a strong case in favor of Cr $K\alpha$ XES as a potential standard test method for the determination of Cr(VI) species fractions in plastics. Several future directions are needed to assess the viability of this proposal and to potentially further improve on the current methodology. First, the Cr $K\beta$ diagram line should be investigated at high energy resolution for the purpose of quantitatively analyzing the Cr(VI) content in the manner of Malherbe et al.²⁵ Second, efforts to extend the practical integration time for PVC materials should explore the use of larger sample areas, cryogenic temperatures, and replicates. Third, the required integration times listed in Table 2 are, at present, prohibitively long for some applications, yet measurements could be greatly accelerated in several ways. First, the tube was operated at only 8 W. It is nearly the lowest powered analytical XRF tube commercially available. Commercial XRF spectrometers come with tube power as high as 4 kW, and even standard 50 and 100 W XRF-style tubes promise 5× to 10× improvements in

measurement time that would suffice for greatly improved throughput. The measurements could be further expedited by increasing the collection solid angle by multiplexing several analyzers or by switching to newly available 0.5 m spherical optics.⁵⁷

CONCLUSION

The Cr(VI) species fraction has been measured via XES and XAFS analysis in a variety of plastic certified reference materials and research samples with at most 8.1% disagreement between the methods. It was demonstrated that XES may be applied to plastics spanning a range of polymer formulations, Cr mass fractions, and Cr(VI) species fractions. The method is nondestructive, requires minimal sample prep, and may be performed with laboratory-based instrumentation. This technique provides quantitative measurements of the Cr(VI) species fraction with uncertainties sufficiently small to permit the application of this procedure toward regulatory compliance concerns. For the above reasons, laboratory-based Cr K α XES measurements have the potential to become industrially relevant as a standard test method.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.8b00302.

Photosensitivity analysis, uncertainty overview, and depiction of instrumentation (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: seidler@uw.edu (G.T.S.).

ORCID

Gerald T. Seidler: 0000-0001-6738-7930

Notes

Certain commercial items are identified in this document to adequately specify experimental procedures. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply the materials or equipment identified are necessarily the best available for the purpose.

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based in part upon work supported by the State of Washington through the University of Washington Clean Energy Institute and by the U.S. Department of Energy through the Chemical Science and Engineering Division of Argonne National Laboratory.

REFERENCES

- (1) Saha, R.; Nandi, R.; Saha, B. *J. Coord. Chem.* **2011**, *64*, 1782–1806.
- (2) Kim, Y. S.; Choi, Y. R.; Kim, J. S.; Ko, J. H.; Park, T. J.; Heo, S. B.; Lim, H. B. *J. Anal. At. Spectrom.* **2015**, *30*, 225–231.
- (3) *Off. J. Eur. Union* **2011**, *54*, 88–110.
- (4) Schulte, P. A.; Rinehart, R.; Okun, A.; Geraci, C. L.; Heidel, D. S. *J. Safety Res.* **2008**, *39*, 115–121.
- (5) Pflaum, R. T.; Howick, L. C. *J. Am. Chem. Soc.* **1956**, *78*, 4862–4866.
- (6) Malherbe, J.; Isaure, M. P.; Seby, F.; Watson, R. P.; Rodriguez-Gonzalez, P.; Stutzman, P. E.; Davis, C. W.; Maurizio, C.; Unceta, N.; Sieber, J. R.; Long, S. E.; Donard, O. F. X. *Environ. Sci. Technol.* **2011**, *45*, 10492–10500.
- (7) Frommer, J.; Nachtegaal, M.; Czekaj, I.; Weng, T. C.; Kretzschmar, R. *J. Phys. Chem. A* **2009**, *113*, 12171–12178.
- (8) Farges, F. *Phys. Chem. Miner.* **2009**, *36*, 463–481.
- (9) Szulczewski, M. D.; Helmke, P. A.; Bleam, W. F. *Environ. Sci. Technol.* **2001**, *35*, 1134–1141.
- (10) Ohata, M.; Matsubayashi, N. *Spectrochim. Acta, Part B* **2014**, *93*, 14–19.
- (11) Goodarzi, F.; Huggins, F. E. *J. Environ. Monit.* **2001**, *3*, 1–6.
- (12) Jiao, F.; Wijaya, N.; Zhang, L.; Ninomiya, Y.; Hocking, R. *Environ. Sci. Technol.* **2011**, *45*, 6640–6646.
- (13) Wells, H. C.; Sizeland, K. H.; Edmonds, R. L.; Aitkenhead, W.; Kappen, P.; Glover, C.; Johannessen, B.; Haverkamp, R. G. *ACS Sustainable Chem. Eng.* **2014**, *2*, 1864–1870.
- (14) Fandeur, D.; Juillot, F.; Morin, G.; Olivi, L.; Cognigni, A.; Webb, S. M.; Ambrosi, J. P.; Fritsch, E.; Guyot, F.; Brown, G. E., Jr. *Environ. Sci. Technol.* **2009**, *43*, 7384–7390.
- (15) Johnson, A. S.; Miseikis, L.; Wood, D. A.; Austin, D. R.; Brahms, C.; Jarosch, S.; Strüber, C. S.; Ye, P.; Marangos, J. P. *Struct. Dyn.* **2016**, *3*, 062603.
- (16) Mortensen, D. R.; Seidler, G. T.; Ditter, A. S.; Glatzel, P. *J. Phys.: Conf. Ser.* **2016**, *712*, 012036.
- (17) Németh, Z.; Szlachetko, J.; Bajnóczi, É. G.; Vankó, G. *Rev. Sci. Instrum.* **2016**, *87*, 103105.
- (18) Seidler, G. T.; Mortensen, D. R.; Remesnik, A. J.; Pacold, J. I.; Ball, N. A.; Barry, N.; Styczinski, M.; Hoidn, O. R. *Rev. Sci. Instrum.* **2014**, *85*, 113906.
- (19) Seres, J.; Seres, E.; Landgraf, B.; Ecker, B.; Aurand, B.; Kuehl, T.; Spielmann, C. *Sci. Rep.* **2015**, *4*, 4234.
- (20) Kucukonder, A.; Sahin, Y.; Buyukkasap, E.; Kopya, A. *J. Phys. B: At., Mol. Opt. Phys.* **1993**, *26*, 101–105.
- (21) Mukoyama, T.; Taniguchi, K.; Adachi, H. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *34*, 3710–3716.
- (22) Tamaki, Y. *X-Ray Spectrom.* **1995**, *24*, 235–240.
- (23) de Oliveira, L.; Antunes, A. M.; Bueno, M. I. M. S. *X-Ray Spectrom.* **2010**, *39*, 279–284.
- (24) Baydas, E.; Oz, E. *X-Ray Spectrom.* **2009**, *38*, 394–398.
- (25) Malherbe, J.; Claverie, F. *Anal. Chim. Acta* **2013**, *773*, 37–44.
- (26) de Groot, F. *Chem. Rev.* **2001**, *101*, 1779–1808.
- (27) Bergmann, U.; Glatzel, P. *Photosynth. Res.* **2009**, *102*, 255–266.
- (28) de Groot, F. *Coord. Chem. Rev.* **2005**, *249*, 31–63.
- (29) Glatzel, P.; Bergmann, U. *Coord. Chem. Rev.* **2005**, *249*, 65–95.
- (30) Ankudinov, A. L.; Elam, W. T.; Sieber, J. R.; Rehr, J. J. *X-Ray Spectrom.* **2006**, *35*, 312–318.
- (31) March, A. M.; Assefa, T. A.; Bressler, C.; Doumy, G.; Galler, A.; Gawelda, W.; Kanter, E. P.; Németh, Z.; Pápai, M.; Southworth, S. H.; Young, L.; Vankó, G. *J. Phys. Chem. C* **2015**, *119*, 14571–14578.
- (32) Nilsson, A.; Pettersson, L. G. M. *Surf. Sci. Rep.* **2004**, *55*, 49–167.
- (33) Deluigi, M. T.; de Groot, F. M. F.; Lopez-Diaz, G.; Tirao, G.; Stutz, G.; de la Vega, J. R. *J. Phys. Chem. C* **2014**, *118*, 22202–22210.
- (34) Deluigi, M. T.; Tirao, G.; Stutz, G.; Cusatis, C.; Riveros, J. A. *Chem. Phys.* **2006**, *325*, 477–484.
- (35) Anklamm, L.; Schlesiger, C.; Malzer, W.; Grötzsch, D.; Neitzel, M.; Kanngießner, B. *Rev. Sci. Instrum.* **2014**, *85*, 053110.
- (36) Dolgih, V. E.; Cherkashenko, V. M.; Kurmaev, E. Z.; Goganov, D. A.; Ovchinnikov, E. K.; Yarmoshenko, Y. M. *Nucl. Instrum. Methods Phys. Res.* **1984**, *224*, 117–119.
- (37) Hoszowska, J.; Dousse, J. C.; Kern, J.; Rhème, C. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1996**, *376*, 129–138.
- (38) Kavčič, M.; Dousse, J. C.; Szlachetko, J.; Cao, W. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2007**, *260*, 642–646.
- (39) Kayser, Y.; Blachucki, W.; Dousse, J. C.; Hoszowska, J.; Neff, M.; Romano, V. *Rev. Sci. Instrum.* **2014**, *85*, 043101.

- (40) Mantouvalou, I.; Witte, K.; Grötzsch, D.; Neitzel, M.; Günther, S.; Baumann, J.; Jung, R.; Stiel, H.; Kanngießer, B.; Sandner, W. *Rev. Sci. Instrum.* **2015**, *86*, 035116.
- (41) Szlachetko, M.; Berset, M.; Dousse, J. C.; Hoszowska, J.; Szlachetko, J. *Rev. Sci. Instrum.* **2013**, *84*, 093104.
- (42) Holden, W. M.; Hoidn, O. R.; Ditter, A. S.; Seidler, G. T.; Kas, J.; Stein, J. L.; Cossairt, B. M.; Kozimor, S. A.; Guo, J.; Ye, Y.; Marcus, M. A.; Fakra, S. *Rev. Sci. Instrum.* **2017**, *88*, 073904.
- (43) *International Electrotechnical Commission*, 1st ed.; Report of the Fourth International Interlaboratory Study (IIS4). IEC 62321-7-2, 2017.
- (44) Ma, L.; Feng, L.; Hioki, A.; Cho, K. H.; Vogl, J.; Berger, A.; Turk, G.; Macleod, S.; Labarraque, G.; Tong, W. F.; Schiel, D.; Yafa, C.; Valiente, L.; Konopelko, L. A.; Quetel, C.; Vermaercke, P.; Manzano, J. V. L.; Linsky, M.; Cort, E.; Tangpitayakul, S.; et al. *Accredit. Qual. Assur.* **2010**, *15*, 39–44.
- (45) Mortensen, D. R.; Seidler, G. T. *J. Electron Spectrosc. Relat. Phenom.* **2017**, *215*, 8–15.
- (46) Engelhard, M.; Krishna, A.; Kulkarni, P.; Lee, C.-Y.; Baer, D. *Surf. Sci. Spectra* **2003**, *10*, 57–66.
- (47) Militello, M. C.; Gaarenstroom, S. W. *Surf. Sci. Spectra* **2003**, *10*, 127–136.
- (48) Mortensen, D. R.; Seidler, G. T.; Kas, J. J.; Govind, N.; Schwartz, C. P.; Pemmaraju, S.; Prendergast, D. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2017**, *96*, 125136.
- (49) Ravel, B.; Newville, M. *J. Synchrotron Radiat.* **2005**, *12*, 537–541.
- (50) Bajt, S.; Clark, S. B.; Sutton, S. R.; Rivers, M. L.; Smith, J. V. *Anal. Chem.* **1993**, *65*, 1800–1804.
- (51) Lytle, F. W.; Greigor, R. B.; Bibbins, G. L.; Blohowiak, K. Y.; Smith, R. E.; Tuss, G. D. *Corros. Sci.* **1995**, *37*, 349–369.
- (52) Sutton, S. R.; Jones, K. W.; Gordon, B.; Rivers, M. L.; Bajt, S.; Smith, J. V. *Geochim. Cosmochim. Acta* **1993**, *57*, 461–468.
- (53) Szulczewski, M. D.; Helmke, P. A.; Bleam, W. F. *Environ. Sci. Technol.* **1997**, *31*, 2954–2959.
- (54) Lytle, F. W.; Greigor, R. B.; Panson, A. J. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 1550–1562.
- (55) Calas, G.; Petiau, J. *Solid State Commun.* **1983**, *48*, 625–629.
- (56) Kendig, M. W.; Davenport, A. J.; Isaacs, H. S. *Corros. Sci.* **1993**, *34*, 41–49.
- (57) Rovezzi, M.; Lapras, C.; Manceau, A.; Glatzel, P.; Verbeni, R. *Rev. Sci. Instrum.* **2017**, *88*, 013108.
- (58) Certificate of Analysis for SRM 2859; National Institute of Standards and Technology, Gaithersburg, MD, <https://www-s.nist.gov/srmors/certificates/2859.pdf>; accessed December 2017.
- (59) Certificate of Analysis for SRM 2861; National Institute of Standards and Technology, Gaithersburg, MD, <https://www-s.nist.gov/srmors/certificates/2861.pdf>; accessed December 2017.
- (60) *European Reference Materials* 2007, Report EUR 22784 EN.
- (61) Ohata, M.; Kurahashi, M.; Hioki, S. *Bunseki Kagaku* **2008**, *57*, 417–426.